2 hours

If you run out of space continue on the back of the page and clearly show which number/part you are referring to.

PROBLEM	SCORE	Max Score
1	17	18
2	15	15
3	14	14
4	13	15
5	14	15
6	11	13
		90

(**Last name,** then first) ███████████

Signature ███████████

ID # ███████████

TA name or discussion section

Kris Barr 3F

Instructions: **This exam has 6 questions plus a periodic table at end of exam. Verify you have the right number of pages before you begin. Different questions carry different numbers of points. Write your name on each page.** Raise your hand if you don't understand a question. **SHOW YOUR WORK!** No credit will be given for an unsubstantiated or illegible answer. Write legibly, use proper units throughout and use significant figures in all answers.

Only use scientific calculators. You cannot use a programmable or graphing calculator or a cell phone or smart phone.

Good luck!

Possibly useful information:

$h = 6.63 \times 10^{-34}$ J sec $\qquad N_0 = 6.02 \times 10^{23}$ mol^{-1} $\qquad c = 3.00 \times 10^8$ m sec^{-1}

$m_e = 9.11 \times 10^{-31}$ kg $\qquad$ 1 a.m.u. $= 1.66 \times 10^{-27}$ kg $\qquad$ 1 Å $= 10^{-10}$ m

$g = 9.81$ m/s $\qquad e = 1.602 \times 10^{-19}$ C $\qquad \varepsilon_0 = 8.854 \times 10^{-12}$ C^{-2}J^{-1}m^{-1}

1 eV $= 1.602 \times 10^{-19}$ J $\qquad V_{electrostatic}(r) \propto Q_1 Q_2 / r;$ $\qquad$ K.E. $= 1/2 mv^2 = p^2 / 2m$

$\lambda v = c$ $\qquad \Delta E = E_f - E_i = e_{photon} = hv$ $\qquad hv = hv_o + $ K. E.(electron)

$\lambda = \dfrac{h}{mv} = \dfrac{h}{p}$ $\qquad m\Delta v \Delta x = \Delta p \Delta x \geq \dfrac{h}{4\pi}$ $\qquad$ Probability density $= |\Psi_n(r)|^2$

$E_n = -(2.18 \times 10^{-18}$ J$)Z^2 / n^2$ $\qquad r_n = (0.529$ Å$)n^2 / Z$ $\qquad a_0 =$ The Bohr radius $= 5.29 \times 10^{-11}$ m

n-l-1 spherical (radial) nodes; $\qquad$ l angular nodes; $\qquad$ n-1 total nodes

Bond order $= $ (# bonding e$^-$ - # antibonding e$^-$)/2
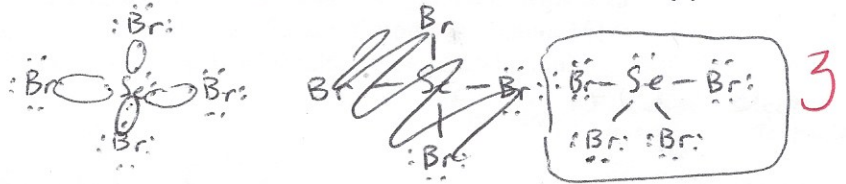
$E_{Coulomb} = q_1 q_2 / (4\pi \varepsilon_0 R)$

$$\bar{r}_{n\ell} = \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$$

Probability $= (\Psi_{nlm})^2 dV = [Rnl(r)]^2 [Y_{lm}(\theta,\varphi)]^2 dV$

$\Psi_{1s} = (Z^3 / \pi a_0^3)^{1/2} e^{-Zr/a_0}$

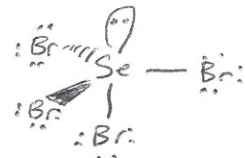**1(a)** Consider the $SeBr_4$ molecule and deduce its Lewis structure. (3)
(show your work)

Valence $e^- = (6) + 4(7) = 34$
Full Shell $e^- = 5(8) = 40$
Bonded $e^- = 40 - 34 = 6e^-$
Lone Pair $e^- = 34 - 8 = 26$

3

1(b) What are the two possible 3-D structures for this molecule? (2)

See-Saw (or Irregular Tetrahedral) | Trigonal Bipyramidal

2

check angles

1(c) For each of the two shapes indicate the type and number of all ten repulsions between pairs of electrons, such as lone pair–bonded pair and give the bond angles concerned in each case. When describing each repulsion assume that no distortions due to lone pair repulsions have occurred yet.

2 instances 93.5°
2 instances 120°

(8) Angle ↑ **7**

Sees-Saw:

Lone Pair–Bonded Pair: 4 instances   93.5°, 120°
Bonded Pair–Bonded Pair: 6 instances   102°/173°

1 instance 173°, 4 instances 102°, 1 instance 120°

Trigonal Bipyramidal:

Lone Pair–Bonded Pair: 4 instances,   Angle 90° 180° 1 instance is 180°, 3 instances are 90°
Bonded Pair–Bonded Pair: 6 instances, ✓   120° 90° →3 of these instances are 120° →3 of these instances are 90°

1(d) The classical expression for the density of black body radiation is

$$\rho_T(\nu) = \frac{8\pi k_B T \nu^2}{c^3}$$

Planck's derived a new expression which featured his constant h.

$$\rho_T(\nu) = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{e^{h\nu/k_B T} - 1}$$

Show how the Planck expression reduces to the classical one when the temperature is very high. (5)

Assume $x = \frac{h\nu}{k_B T}$
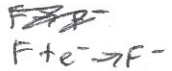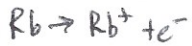
5

At high temperatures $e^x \sim 1 + x$

$$\rho_T(\nu) = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{e^x - 1}$$

$$\rho_T(\nu) = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{(1+x) - 1} = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{x}$$

$$= \frac{8\pi h \nu^3}{c^3} \cdot \frac{k_B T}{h\nu}$$

$$\boxed{\rho_T(\nu) = \frac{8\pi k_B T \nu^2}{c^3}}$$ which matches the classical expression.

/17

2(a). In a gaseous RbF molecule the bond length is 2.274 x 10⁻¹⁰ m. Using the following data estimate the dissociation energy of this molecule into Rb and F atoms in kJ/mol. (6)
First ionization energy of Rb = 403.0 kJ/mol, Electron affinity of F = 328.0 kJ/mol
(defined as $F^- \rightarrow F + e^-$)

$E_{transfer} = \text{Ionization Energy} - \text{Electron Affinity}$

$Rb \rightarrow Rb^+ + e^-$

$F + e^- \rightarrow F^-$

$E_{coulomb} = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r} = \dfrac{(1.602\times10^{-19} C)^2}{4\pi(8.854\times10^{-12} c^2 J^{-1} m^{-1})(2.274\times10^{-10} m)}$

$E_{Dissociation} = E_{coulomb} - E_{transfer}$

$= (610.6 \frac{kJ}{mol}) - (75.0 \frac{kJ}{mol})$

Dissociation Energy = $535.6 \frac{kJ}{mol}$

$= (403.0 \frac{kJ}{mol}) - (328.0 \frac{kJ}{mol})$

$E_{transfer} = 75.0 kJ/mol$

$\dfrac{(1.014\times10^{-18} J)}{1} \times \dfrac{1 kJ}{1\times10^3 J} \times \dfrac{6.02\times10^{23} e^-}{1 mol} = 610.6 kJ/mol$

6

2(b) Explain the term "ad hoc" as it applies to scientific theories and give an example to illustrate how your example was ad hoc. (4)

"Ad hoc" is when certain conclusions are made or formulas are created just because they work, not because of natural derivation or evidence. (So they were unnaturally forced into theories of equations) An example is Bohr adding quantization to his model or the 4th quantum number being given its values; they weren't naturally occurring, but were added just because they worked and helped people make sense of things (although they could later be derived naturally).

4

2(c) Explain what happens when a beam of rapidly moving electrons is fired at a 2-slit arrangement. This beam consists of millions of electrons per second. (2)

The electrons act like waves and diffraction occurs, creating an interference pattern on the screen the electrons are projected on, so destructive interference and constructive interference occur.

2

2(d) How does the pattern change if the electron beam consists of one electron per every 10 seconds. Why is it difficult to understand this pattern or different from what you might expect (3)

An interference pattern arises (develops gradually or slowly) on the screen, and this is odd because the electrons enter one slit at a time, and so it's odd because interference typically needs two things interacting with each other, while in this case there's only one electron at a time fired, so the question is what does it interact with or what properties create the interference pattern? You would expect the electrons to just pile up. electrons to just pile up

3

15

3(a) Calculate the frequency of light when (i) a C^{5+} undergoes a transition from the n = 3 to the n = 6 orbit. Explain why the sign of the energy is either positive or negative. (5)

$$\Delta E = E_6 - E_3 \qquad\qquad E_n = (-2.18\times10^{-18}J)\frac{Z^2}{n^2}$$

$$= (-2.18\times10^{-18}J)\left(\frac{6^2}{6^2} - \frac{6^2}{3^2}\right) \quad E = h\nu$$

$$\boxed{\Delta E = 6.54\times10^{-18}J} \longrightarrow \nu = \frac{E}{h} = \frac{(6.54\times10^{-18}J)}{(6.63\times10^{-34}Js)} = \boxed{9.86\times10^{15}Hz} = \text{frequency of light}$$

The sign is positive because energy must be absorbed as the C^{5+} undergoes a transition from a shell of high stability to lower stability.

5

3(b) Sketch a graph to show the variation in first ionization energy with atomic number for the third period (Na to Ar). Include any anomalies. (3)
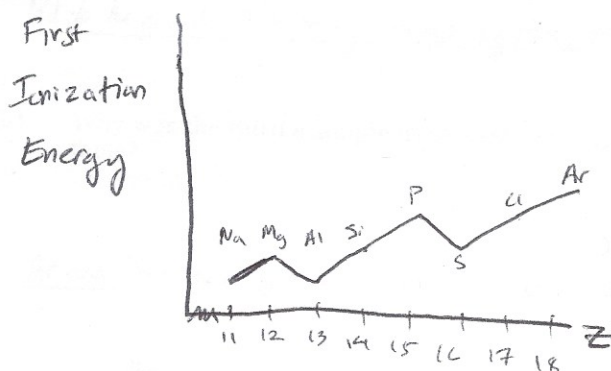
Ionization energy typically increases as you go across the period. The anomalies are seen between Mg and Al, and P and S where the ionization energies decrease rather than increase.

3

3(c) Give an explanation for the overall trend and for the anomaly which occurs between groups V and VI. Diagrams may be included. (6)

6

Ionization energy typically increases as you go across a period because the effective nuclear charge of the atom increases, meaning that it requires more energy to remove a valence electron. The group V - group VI anomaly occurs because S has two electrons in one of its orbitals, meaning there's electrostatic repulsion, while P has no orbitals with two electrons and it is easier to remove an electron from S because of this repulsion.

Diagram:
P
↑ ↑ ↑ | S ↑↓ ↑ ↑
3p   3p
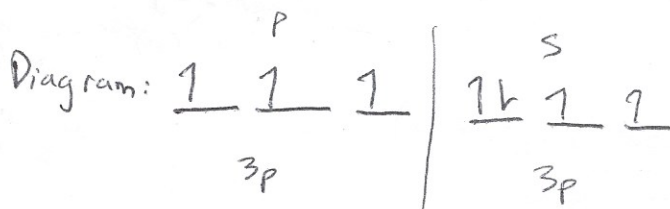
/14

4(a) Explain the significance of the following sets of 2 elements in the development of the periodic table,

Co, Ni.   Te, I.   Ar, K   (3)

The periodic table was originally arranged by $\overset{\text{increasing}}{\vee}$ atomic mass, but these sets of 2 elements

caused problems because even though Co comes before Ni in the periodic table, Co has a higher

The same concept applies to Te, I and Ar, K

atomic mass than Ni. This is due to isotope prevalence and atomic mass being a weighted average. This

3/3

led to the periodic table being arranged by atomic number $\overset{\text{instead of atomic mass}}{^}$ to correct the order and reaffirm periodic trends.

4(b) Why was the third example irrelevant to the chemists who first developed the periodic table? (2)

Ar and K were irrelevant because these chemists didn't put the noble gases (like

0/2

Ar) on $\overset{\text{their}}{^}$ the periodic table.

4(c) Calculate the average distance of an electron from the nucleus in the case of a 3d orbital. (He⁺) (5)

$$\overline{r}_{ne} = \frac{n^2 a_0}{z}\left\{1 + \frac{1}{2}\left[1 - \frac{l(l+1)}{n^2}\right]\right\} \qquad l = 2 \qquad z = 2$$
$$n = 3$$

$$= \frac{3^2(5.29\times10^{-11}m)}{2}\left\{1 + \frac{1}{2}\left[1 - \frac{2(2+1)}{3^2}\right]\right\}$$

5/5

$$= \frac{3^2(5.29\times10^{-11}m)}{2}\left\{1 + \frac{1}{2}\left[1 - \frac{6}{9}\right]\right\}$$

$$\boxed{\overline{r}_{ne} = 2.78\times10^{-10}m} = \text{average distance of an electron from the nucleus in this case}$$

Using He⁺

4(d) Calculate the probability of finding an electron in a 1s orbital in a sphere of volume $(10^{-10}$ m$)^3$ at a distance of 3 Bohr radii from the nucleus. (5)

$$\text{Probability} = \psi^2 dV \qquad \text{Probability} = \left[\left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-6}\right]^2 (10^{-10}m^3)^3$$

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-zr/a_0} \qquad z = 2$$
$$a_0 = 5.29\times10^{-11}m$$

$$= \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-2(3a_0/a_0)} \qquad = \frac{1.06\times10^{26}}{m^3}(10^{-30}m^3)$$

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-6} \qquad \text{Probability} = 0.000106$$

5/5

$$\text{or} \quad \boxed{0.0106\%}$$

14

5(a)   Suppose you want to demonstrate the interference of microwaves with a frequency of 500 Mega Hz. (Mega means one million). What is the approximate slit width that would be needed to do this?   (2)

$$\lambda = \frac{c}{v} = \frac{(3.00 \times 10^8 \, m/s)}{(500 \, MHz \times \frac{1 \times 10^6 \, Hz}{1 \, MHz})} = 6.00 \times 10^{-1} \, m$$

The slit width would have to be about 0.600 m.

Slit width ~ magnitude of λ

2

5(b)   The original Bohr model described the configurations of atoms using just one quantum number, n. There were no subshell or orbitals in the modern sense. Give diagrams to show each of the following atoms in the Bohr model. Indicate each shell and the number of electrons they contain   (3)

calcium   boron,   phosphorus

n=4 2e⁻
n=3 8e⁻
n=2 8e⁻
n=1 2e⁻

n=2 3e⁻
n=1 2e⁻

n=3 5e⁻
n=2 8e⁻
n=1 2e⁻

3
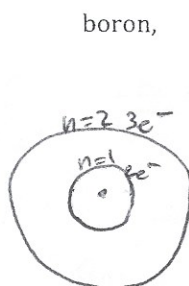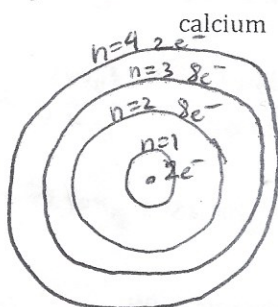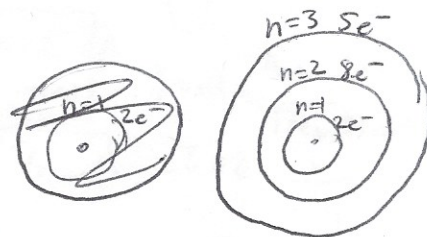
5(c)   Now give the detailed configuration according to the use of four quantum numbers. Do this using spectroscopic notation such as $1s^2$ $2s^1$ etc. and show the relevance of Hund's rule, if any, by means of labels such as p_x etc.   (6)

Calcium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Boron: $1s^2 2s^2 2p_x^1$

Phosphorous: $1s^2 2s^2 2p^6 3s^2 3p_x^1 2p_y^1 2p_z^1$

6

5(d)   Explain why the last four electrons to occupy the orbitals in an atom of titanium go into 3d orbitals first and then 4s. Also comment on the ionization of this atom   (4)

For titanium, 3d orbitals have less energy than 4s orbitals, and according to Aufbau's Principle,

electrons fill the lowest orbitals first, so the last four electrons fill the 3d orbital then the 4s orbital.

The 4s orbital will lose electrons first in ionization because the last orbital to fill has the first electrons

removed, and the 4s orbital is less stable than the 3d orbital, so electrons are removed from 4s first

15

6. (a) The percentage yield for the following reaction is 56.0%.

$$Br_2 \quad + \quad I_2 \quad \longrightarrow \quad 2\ BrI$$

What amount of BrI is formed from the reaction of 0.025 kg of Br_2 with 0.025 kg of I_2? Molar Mass $Br_2 = (79.904)2 = 159.808\ g/mol$ Molar Mass $I_2 = 2(126.905) = 253.81\ g/mol$ (6)

$\dfrac{0.025\ kg\ Br_2}{1} \times \dfrac{1\times10^3\ g}{1\ kg} \times \dfrac{1\ mol\ Br_2}{159.808\ g} = 0.16\ mol\ Br_2$ coefficient in balanced reaction

$0.16\ mol\ Br_2 \div 1 = 0.16\ mol\ Br_2$

$\dfrac{0.025\ kg\ I_2}{1} \times \dfrac{1\times10^3\ g}{1\ kg} \times \dfrac{1\ mol\ I_2}{253.81\ g} = 0.098\ mol\ I_2$ $0.098\ mol\ I_2 \div 1 = 0.098\ mol\ I_2$ ← Limiting because Reactant

$0.098\ mol\ I_2 < 0.16\ mol\ Br_2$

$\dfrac{0.025\ kg\ I_2}{1} \times \dfrac{1\times10^3\ g}{1\ kg} \times \dfrac{1\ mol\ I_2}{253.81\ g} \times \dfrac{2\ mol\ BrI}{1\ mol\ I_2} \times \dfrac{206.809\ g}{1\ mol\ BrI} = 41\ g\ BrI$ formed

Molar Mass $BrI = 79.904\ g + 126.905\ g = 206.809\ g/mol$

$22.3\ g\ BrI$ formed $\times 2$ → Answer

% Yield = $\dfrac{Actual}{Theoretical}$ $56.0\% = \dfrac{y}{41\ g}$

(b) What amount of the excess reagent (in kg) is left unchanged? (2)

$\dfrac{0.025\ kg\ I_2}{1} \times \dfrac{1\times10^3\ g}{1\ kg} \times \dfrac{1\ mol\ I_2}{253.81\ g} \times \dfrac{1\ mol\ Br_2}{1\ mol\ I_2} \times \dfrac{159.808\ g}{1\ mol\ Br_2} \times \dfrac{1\ kg}{1\times10^3\ g} = 0.016\ kg\ Br_2\ used$

Excess Reagent = $0.025\ kg - 0.016\ kg = $ $0.009\ kg$ left unchanged of Br_2

(c) A 2.00 g sample of a compound containing C, H and O only gave 4.86 g of CO_2 and 2.03 g of H_2O on complete combustion. Find the empirical formula. (5)

Molar Mass $CO_2 = 12.011 + 2(15.999) = 44.009\ g/mol$

Molar Mass $H_2O = 2(1.0080) + 15.999 = 18.015\ g/mol$

Mass C: $\dfrac{4.86\ g\ CO_2}{1} \times \dfrac{1\ mol\ CO_2}{44.009\ g} \times \dfrac{1\ mol\ C}{1\ mol\ CO_2} \times \dfrac{12.011\ g}{1\ mol\ C} = 1.33\ g\ C$

Mass H: $\dfrac{2.03\ g\ H_2O}{1} \times \dfrac{1\ mol\ H_2O}{18.015\ g} \times \dfrac{2\ mol\ H}{1\ mol\ H_2O} \times \dfrac{1.0080\ g}{1\ mol\ H} = 0.23\ g\ H$

Mass O = Mass Sample − Mass C − Mass H

$= 2.00\ g - 1.33\ g - 0.23\ g = 0.44\ g\ O$

mol C: $\dfrac{4.86\ g\ CO_2}{1} \times \dfrac{1\ mol\ CO_2}{44.009\ g} \times \dfrac{1\ mol\ C}{1\ mol\ CO_2} = 0.110\ mol\ C$ $\dfrac{0.110\ mol}{0.028\ mol} \approx 4$

mol H: $\dfrac{2.03\ g\ H_2O}{1} \times \dfrac{1\ mol\ H_2O}{18.015\ g} \times \dfrac{2\ mol\ H}{1\ mol\ H_2O} = 0.225\ mol\ H$ $\dfrac{0.225\ mol}{0.028\ mol} \approx 8$

mol O: $\dfrac{0.44\ g\ O}{1} \times \dfrac{1\ mol\ O}{15.999\ g} = 0.028\ mol\ O$ $\dfrac{0.028\ mol}{0.028\ mol} = 1$

Empirical Formula: C_4H_8O